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DOI:

[10.1016/j.foodhyd.2015.11.020](https://doi.org/10.1016/j.foodhyd.2015.11.020)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Hamilton, I & Norton, I 2016, 'Modification to the lubrication properties of xanthan gum fluid gels as a result of sunflower oil and triglyceride stabilised water in oil emulsion addition', *Food Hydrocolloids*, vol. 55, pp. 220-227. <https://doi.org/10.1016/j.foodhyd.2015.11.020>

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Checked for eligibility 10/02/2016

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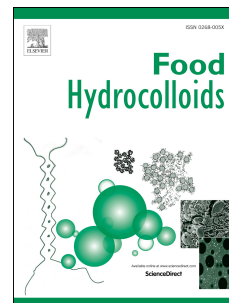
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Accepted Manuscript

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PII: S0268-005X(15)30152-1

DOI: [10.1016/j.foodhyd.2015.11.020](https://doi.org/10.1016/j.foodhyd.2015.11.020)

Reference: FOOHYD 3200

To appear in: *Food Hydrocolloids*

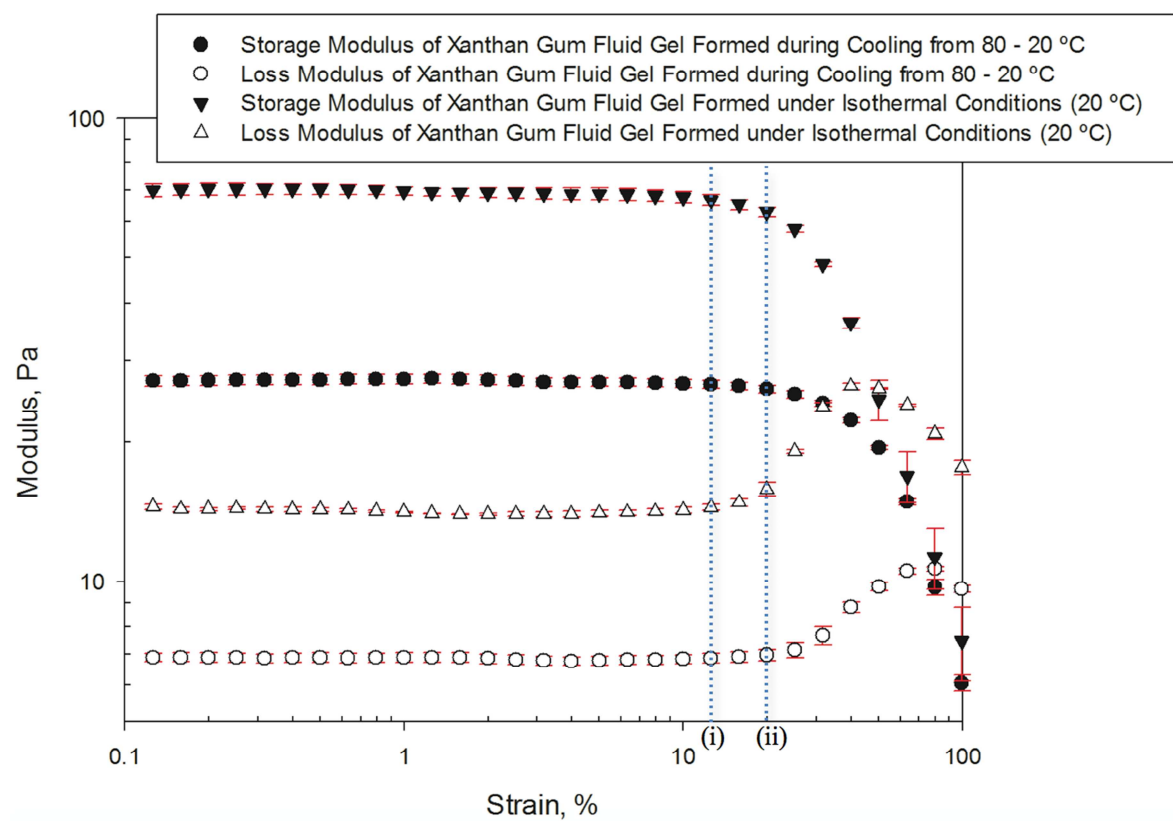
Received Date: 4 August 2015

Revised Date: 9 November 2015

Accepted Date: 14 November 2015

Please cite this article as: Hamilton, I.E., Norton, I.T., Modification to the lubrication properties of xanthan gum fluid gels as a result of sunflower oil and triglyceride stabilised water in oil emulsion addition, *Food Hydrocolloids* (2015), doi: 10.1016/j.foodhyd.2015.11.020.

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Modification to the Lubrication Properties of Xanthan Gum Fluid Gels as a Result of Sunflower Oil and Triglyceride Stabilised Water in Oil Emulsion Addition

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Abstract

A range of xanthan gum fluid gels and fluid gel emulsion mixtures have been constructed and their lubrication behaviour compared to high oleic sunflower oil. In addition, the lubrication properties have been measured after the addition of oil to the fluid gel, along with the effect of dispersing 10 % (wt/wt) of a stabilised and un-stabilised oil continuous emulsion into the fluid gel postproduction.

This study has highlighted a method of producing xanthan gum fluid gels as well as a fat mimetic formulation based on a xanthan gum fluid gel/oil formulation, which has lubrication properties equivalent to that of standard sunflower oil during soft tribology experiments. The final formulation was shown to have similar initial lubrication behaviour as sunflower oil with a 93 % oil reduction.

Keywords:

Fluid gel, Fat replacement, Lubrication, Sunflower oil, Xanthan gum, Fat mimetic

1. Introduction

The presence of fats is a vital component in foodstuffs due to its contribution to oral properties such as flavour, palatability, mouth feel and lubrication. (de Wijk, Terpstra, Janssen, & Prinz, 2006; O'Quinn, et al., 2012) The consumption of excessive quantities of dietary fat has been shown to increase the risk of medical conditions such as obesity, high blood pressure and coronary heart disease. (Willett, 2012) The food industry in an attempt to facilitate healthier diets has adopted several methods of fat replacement. One such method is the use of hydrogels with lipid-like properties. Hydrocolloids are increasingly becoming key components in food industry formulations and have been widely discussed as potential systems in fat reduction/replacement applications. (Farres, Moakes, & Norton, 2014; Gidley, 2013) In order to be successful in emulating the attributes of fat systems, it is

important to gain an understanding of the lubrication behaviour of these systems so that the impact of fat reduction on oral perception is minimised. (Selway & Stokes, 2013)

The disruption of the molecular ordering of a biopolymer during its gelation is the primary method of forming fluid gel systems. (Cassin, Appelqvist, Normand, & Norton, 2000; Garrec, Frasc-Melnik, Henry, Spyropoulos, & Norton, 2012) A method commonly used is the application of shear forces to the gelling mixture leading to the separation of gel nuclei's, limiting aggregation. (Farres, Douaire, & Norton, 2013; Garrec & Norton, 2012) Xanthan gum is a naturally occurring polysaccharide widely used as a thickening/stabilisation agent in the food, cosmetic and pharmaceutical industries due to its highly pseudoplastic behaviour. (Fitzpatrick, Meadows, Ratcliffe, & Williams, 2013; Sworn, 2009)

The production of fluid gels that possess properties similar to that of oil emulsion systems is a viable method of fat replacement but unfortunately, the vastly different oral perception of water/gels to that of oil means that fat replacement systems of this type can be easily distinguished from their full fat counterparts, necessitating the inclusion oil into formulations. (Chojnicka-Paszun, de Jongh, & de Kruif, 2012; Nishinari, 2006; van Aken, Vingerhoeds, & de Wijk, 2011)

This study aims to investigate the production of xanthan gum fluid gels and how the rheological behaviour differs from xanthan gum hydrated and sheared at room temperature. Once produced the effect of the addition of sunflower oil on the lubrication behaviour of the xanthan gum fluid gels is shown. Comparisons between sunflower oil and xanthan gum formulations where oil dispersed around the particles have been measured by ball on disk tribology. Finally, the effect on lubrication the mixing of a 30 % water in oil (w/o) triglyceride stabilised emulsion system into the fluid gel postproduction was assessed.

2. Materials and methods

2.1. Materials

The sodium form of xanthan gum was obtained from MH Foods, Nile red was purchased from Sigma-Aldrich, and sunflower oil was obtained from a generic source. Glyceryl monostearate (Dimodan HP Kosher), Tri-palmitate (Edenor C16-98 MY), and Polyglycerol Polyricinoleate were provided from Danisco, Emery Oleochemicals, and Palsgaard, respectively. All materials were used as received and without further purification.

2.2. Methods

2.2.1. Xanthan gum fluid gel production.

Dry pre-weighted xanthan gum powder (1.5 % wt/wt) was added slowly and under constant agitation to heated distilled water (approximately 80 ± 5 °C). The pre gel solution was kept isothermal (above the literature ordered-disordered transition temperature) until complete hydration was achieved, then stirred for a further 30 minutes under cover to prevent evaporative losses. (Mannion, et al., 1992)

Xanthan gum fluid gels were produced by flowing the pre-gel solution through a thermally controlled pin stirrer set to a shaft rotation speed of 2000 rpm (schematic shown in **Fig. 1.**).

The pin stirrer consists of a rotor shaft with evenly distributed pins along its length, which is inserted into a thermally controlled jacket with stators running the length of the inside wall. The arrangement is such that when assembled the rotor pins are positioned between the stator pin of the jacket. In operation, areas of high shear are developed in the gaps between the pins when the centre shaft is rotated. Further details of the construction of the pin stirrer is described in Garrec *et al.* (Garrec & Norton, 2012) For fluid gel production, prior to being subjected to the shear field the fluid temperature remained at $\sim 80\text{ }^{\circ}\text{C}$ and was reduced to $20\text{ }^{\circ}\text{C}$ during transit through the unit. The reduction in temperature provided the driving force for ordering whilst the shear between pins limited overall gelation of the solution volume as a whole.

2.2.2 Water /Oil Emulsion Production (w/o)

As described by Frasch-Melnik *et al.* and Garrec *et al.* particulate emulsions were produced by pumping the pre-emulsion (at a flow rate of 150 ml min^{-1}) through a jacketed scraped surface heat exchanger, followed by a pin stirrer, both of which were set to a shaft rotation speed of 2000 rpm and cooled to $5\text{ }^{\circ}\text{C}$ with water. (Frasch-Melnik, Norton, & Spyropoulos, 2010; Frasch-Melnik, Spyropoulos, & Norton, 2010; Garrec, Frasch-Melnik, et al., 2012) Prior to production, a mixture of nucleation agent (Glyceryl monostearate, 1%), solid fat (Tri-palmitate, 3 %) and emulsifier (PGPR, 1 %) were added to the oil phase, and the bulk temperature raised to ca. $95\text{ }^{\circ}\text{C}$. Once the oil reached the required temperature and a homogeneous dissolution was obtained, water (heated to $60\text{ }^{\circ}\text{C}$) was added to the stirring oil mixture to produce a pre-emulsion that was 30 % w/o (by mass). This pre-emulsion was maintained at $80\text{ }^{\circ}\text{C}$, before being pumped firstly through both the units, collected then passed through the system a second time at the same rate, in order to induce fat network break-up and reduce the particle size of the final emulsion.

2.2.3. Characterisation

Optical light microscopy, Light microscopy was performed using a Brunel SP300-fl (Brunel Microscopes Ltd, UK) fitted with a DSLR camera (Cannon EOS Rebel XS, DS126 191). For the purpose of imaging particles 20x or 40x objective lens were used. Post image processing was made using the software package ImageJ.

Confocal scanning laser microscopy (CLSM), CLSM was performed using a Leica TCS-SPE (Leica DM2500, Leica Microsystems Ltd, UK) fitted with an argon laser. Lipid based particles and sunflower oil were dyed with Nile red. Dyes were excited at 488 nm and detected between 500-550 nm, and image slices were collected at $1\text{ }\mu\text{m}$ intervals through the samples under 40x magnification.

UV transparent/fluorescence free immersion oil (Sigma-Aldrich, UK) was placed between the lenses and coverslip of the sample slide during imaging. Image processing was made using the software package ImageJ.

2.2.4 Rheology measurements

Oscillatory measurements, Storage and loss modulus measurements were made at 20 °C using a Kinexus pro rotational rheometer (Malvern instrument, UK) with a parallel plate geometry (diameter 60 mm, gap set to 1 mm) calibrated with pure water (at 20 °C). Solution of xanthan gum fluid gel and gels hydrated at 20 °C were transferred to the geometries, and the temperature allowed to equilibrate for 5 minutes. The percentage strain on the sample was varied between 0.1 and 100 %. All measurements were made at 1 Hz in triplicate and the average reported on a plot of modulus versus strain percent.

Viscosity measurements during production of fluid gel and gels hydrated at 20 °C, Single shear viscosity measurements during fluid gel production were made using a Kinexus pro rotational rheometer (Malvern instrument, UK) with a vane geometry (internal cup diameter 27 mm, vane rotor 25 mm) calibrated with water (at 20 °C). The required mass of deionised water was added to the vane and the temperature allowed to isotherm either at 20 °C or 80 °C depending on experiment type. Dry powdered xanthan gum was added slowly to the vane under shear (500 s^{-1}) and allowed to mix for 60 minutes. In experiments where the temperature was set to 20 °C, shearing continued for a further 30 minutes. Where the temperature was reduced for 80 °C, the gel temperature was reduced at a cooling rate of 2 °C min^{-1} to 20 °C over a period of 30 minutes under the same shearing rate (500 s^{-1}). All measurements were made in triplicate and the average reported on a plot of viscosity versus time.

Viscosity measurements of final fluid gels and gels hydrated at 20 °C, Viscosity measurements as a result of shear rate were made at 20 °C using a parallel plate geometry (diameter 60 mm, gap set to 1 mm) calibrated with water (at 20 °C). Finished samples were prepared in a pin stirrer either by shearing isothermally or during cooling and tested 48 hours after production. Measurements were made between 0.01 and 500 s^{-1} . All measurements were made in triplicate and the average reported on a plot of viscosity versus shear rate.

2.2.5 Soft tribology

As in Garrec *et al.* (2012) lubrication (expressed as friction coefficient, μ) was recorded as the result of the normal and tangential forces ($\mu = F/W$) using a Mini Traction Machine (MTM, PCS Instruments, UK). (Garrec, Frasc-Melnik, et al., 2012) In order to give results more representative of lubrication in oral processing between a hard and soft surface, similar to the work of Malone *et al.* (2003) typical hard surface was represented using a $\frac{3}{4}$ inch stainless steel ball (AISI 400) (PCS

instruments, UK) coupled with a Polydimethylsiloxane (PDMS) (Samco Silicone Products, UK) disk used for the soft surface. (Malone, Appelqvist, & Norton, 2003) Stribeck curves were obtained when $W =$ between 0.5 and 6N, and measurements taken as the average of the entrainment speed (U) shown in **Eq. 1**, being raised from 1 to 1000 mm s⁻¹ three times. During these experiments the slide-to-roll ratio (SRR) calculated by **Eq. 2** was equal 50 % and defined as:

$$U = \frac{(V_{Ball} - V_{Disk})}{2} \quad (1)$$

$$SRR = \frac{V_{Ball} - V_{Disk}}{U} \quad (2)$$

Each measurement reported was plotted from triplicate measurements of each sample type.

3. Results and discussion

3.1 Gel Particle production

A combination of optical and confocal microscopy (CLSM) was used to confirm, that fluid gel particles had been formed. Microscopy of xanthan gum gels formed after hydration then shearing in the pin stirrer at room temperatures (20 °C) and those hydrated at 80 °C then sheared in the pin stirrer whilst cooling from 80 – 20 °C highlighted a significant difference in the particle shapes and sizes of the final gels (**Fig. 2.**).

When gels were sheared at 20 °C the resultant gel particles were shown to be angular and strongly resembled broken quiescent gel fragments (**Fig. 2a**). When sheared during cooling the fluid gel particles were rounded (**Fig. 2b**). This change in particle shape is probably the result of the application of shear confining the xanthan gum polymer whilst undergone a conformational transition from a disordered coil to a ordered helix. (Garcia-Ochoa, Santos, Casas, & Gomez, 2000; Milas & Rinaudo, 1986; Morris, Lanson, & Turner, 1982) In the samples made at 20 °C the helical xanthan gum chains appeared to be too ridged and “rod-like” to be able to be manipulated into particles by the shear forces alone, on cooling while shearing the more flexible single coiled chains present above the transition temperature was shown to be far more susceptible to manipulation.

The mechanism for 1.5 % (wt/wt) xanthan gum fluid gel production and stabilisation proposed is highlighted below:

1. Hydration of the xanthan gum occurs in the heated solution to bring about the helix-coil transition of the biopolymer

2. The denatured xanthan is then able to align to a greater extent, exposing a greater number of small segments where junction zones can be formed. At these junctions, interaction between the glucose and mannose side chains and the sterically compatible cellulose backbone of other xanthan chains can occur to form discrete xanthan aggregates as reported by Southwick *et al.* (1980). A similar methodology of biopolymer compatibility to that reported in the works of Carins *et al.* (1986) for xanthan gum carob gum mixtures. (Cairns, Miles, & Morris, 1986; Southwick, Lee, Jamieson, & Blackwell, 1980)
3. The size and concentration of xanthan gum in the particle can then grow to the maximum size permitted by the turbulent shear environment, and the excess biopolymer is redispersed to polymer deficient areas
4. Stabilisation of the particles is thought to occur whilst the biopolymer backbone still has flexibility, the negatively charged side chains undergo electrostatic repulsions. The process can then lead to increased packing and/or hindering the remaining small junction zones preventing further entanglement. (Southwick, Jamieson, & Blackwell, 1982) Once back in the ordered conformation, the particle formation is complete and weak interactions between particles is reduced due to potentially a greater number of negatively side chains being exposed, leading to the reduction in storage modulus observed in **Fig 3**.

Investigations are still on going to understand, if the mechanism is the same for xanthan gum as reported by Frith *et al.* (2002) and Garrec *et al.* (2012) in kappa-carrageenan systems where the production temperature and biopolymer concentration could be used to control and tailor properties like particle stiffness and stability during fluid gels production.

Changes in storage and loss modulus of xanthan gum as a result of formation temperatures, Changes in storage and loss modulus of xanthan gum gels that had been formed at 20 °C and those formed whilst cooling from 80 – 20 °C were measured. The comparison is shown in **Fig. 3**.

A significant difference was recorded in both the storage and loss modulus between gels formed under shear isothermally at 20 °C (**Fig. 3**, triangles) and those formed whilst shearing as the temperature was reduced from 80 °C to 20 °C (**Fig. 3**, circles). Under isothermal conditions a bulk storage modulus of 69.7 ± 1.5 Pa, was measured compared to 27.84 ± 0.2 Pa when the gels were prepared as the temperature was reduced (value taken at 1 % strain). A similar difference was noticed in the loss modulus where isothermally hydrated gels of 14.07 ± 0.06 Pa compared to those formed during cooling of 6.9 ± 0.17 Pa (value taken at 1 % strain). Results showed a 60 % reduction in the gel strength for gels prepared during temperature reduction compared to those prepared under isothermal conditions, indicating a reduction in the particle-particle interactions as a consequence of stabilisation brought about by the shearing processes. A 7 % decrease in the gels resistance to deformation was also

recorded for the fluid gel formed during cooling in respect to the isothermal formation (**Fig. 3.** ii and i, respectively), further indicating the reduction in molecular ordering of the biopolymer. The rheological properties developed by the production of the fluid gel, rather than those of gels hydrated and sheared at 20 °C meant that the xanthan gum sheared as the temperature was reduced exhibited more emulsion like behaviour, thought to be vital for mimetic materials

Changes in the viscosity of xanthan gum gels were measured during the hydration at 20 °C under shear (500 s^{-1}) and during the hydration at 80 °C then cooling to 20 °C whilst being subjected to shear (500 s^{-1}). The comparison is shown in **Fig. 4.**

A constant rise in viscosity was observed as xanthan gum powder was hydrated at 80 °C (**Fig. 4.** open triangles). As the temperature was reduced after 3600 minutes and the literature helix-coil temperature of the polymer (Mannion, et al., 1992) was reached (shown by the red arrow in **Fig. 4.**) the viscosity increase ceased and a reduction in the viscosity occurred, this reduction being a result of the formation of discrete particles (fluid gels). Once formed the particle–particle interaction of the xanthan gum gel was reduced resulting in the constant viscosity values (0.0325 ± 0.001) seen at the end of the test in the fluid gel trace (**Fig. 4.** open triangles). The reduction in viscosity in fluid gel systems seen below the transition temperature of gels produced under shear has been described previously in the work of Gabriele *et al.* (2009) in kappa-carrageenan systems as a result of demixing caused by polymer rich and polymer poor regions. (Gabriele, Spyropoulos, & Norton, 2009) These observations are in agreement with the fluid gel formation method proposed earlier in this paper where once xanthan chains have been entangled at the exposed junctions zones in the flexible coil state and repulsive forces have lead to the biopolymer adopting the most thermodynamic stable arrangement, the return to the ridge helix conformation then restricts further mobility in the backbone isolating the negative side chains, resulting in repulsion between the newly formed gel particles, and aiding demixing of the un-entangled polymer chains.

The continual gain in viscosity seen when the xanthan gum was formed at 20 °C under shear at 500 s^{-1} (shown by solid circles in **Fig. 4.**) showed the hydration and subsequent interaction by hydrated particles was unaffected by the shear field whilst the biopolymer was in the ridged form, necessitating the need for the thermal treatment in the production of the fluid gel.

Measurement of the fluid gels viscosity as a result of the applied shear rate after a period of 48 hours had past is shown in **Fig. 5.**

The fluid gels formed whilst cooling thought the transition temperature were shown to have lower values of bulk viscosity compared to those formed isothermally. Both gels exhibited shear-thinning behaviour although the overall reduced bulk viscosity values at all shear rates in the fluid gels formed

during cooling were in agreement with the increased stabilisation as a result of forming a xanthan gum fluid gel. The sustained difference in viscosity values (after 48 hours) also gave evidence that the production method did not form a state in which rheological properties of the fluid gel were only temporary, although the length of stability of these gel structures is still under investigation.

Fluid gels particulate w/o emulsion mixtures

The addition of 10 % wt/wt of triglyceride stabilised emulsion to the fluid gel was investigated. In other published work by the authors, the use of the stabilised emulsion (30/70 water in oil) was shown to give values of friction close to those of sunflower oil alone during rolling friction tests. (Akash Beri, 2015) The benefit of using emulsions as lubrication modifiers as opposed to oil alone was shown to be that these microstructures could use water to replace the overall oil content by 30 % (by mass). Emulsion droplets were dispersed in the fluid gel mixture postproduction CSLM was then used to identify the composition of the dispersed phase of the fluid gel. Upon emulsification it was evident (from the resultant images – **Fig. 6.**) that higher concentration of the Nile red were incorporated into the triglyceride during solidification and in turn resulted in a distinctive contrast between fat shell particles, oil in the system, and the non-stained fluid gel particles. The confocal images of the composite mixtures can be seen in **Fig. 6.**

It was evident by the dyed areas that the oil and emulsion droplets were well dispersed in the aqueous continuous phase and may aid in the overall reduction of friction by lubricating particle-particle interactions or facilitating the separation of the ball and disk surfaces.

3.2 Measurements of lubrication of fluid gels by tribology

Friction measurements were made of water and sunflower oil as a comparison to fluid gels and fluid gel/emulsion mixed systems. **Fig. 7.** Shows the comparison of sunflower oil and water to the fluid gel alone, and when 10 % sunflower oil had been dispersed into the continuous phase of the fluid gel (labelled “Fluid gel – 10 % oil suspension” in the figure).

Aside from sunflower oil there was no evidence that the systems reached hydrodynamic conditions before 1000 mm s^{-1} (shown by the increase in traction at high entrainment speeds), due to the entrainment speed being insufficient to fully suspend particles of the fluid gel particles in the entrained fluid. All formulations showed reduced overall friction in comparison to that of water, with the friction values of the fluid gel only systems all exhibited values higher than sunflower oil for all entrainment speeds. Differences in the limit of boundary lubrication (taken at a point where the values of friction are no longer constant) were also evident in the different formulations. Sunflower oil was shown to overcome boundary conditions at entrainment speeds around 1.5 mm s^{-1} , in comparison,

fluid gel only systems were shown to exhibit lower friction than water and to enter the mixed regime at entrainment speeds above 7 mm s^{-1} , whereas fluid gel oil suspensions were shown to overcome boundary conditions at 4.5 mm s^{-1} (**Fig. 7 blue arrows**). The measured friction values of the fluid gel being significantly lower than water suggesting that the entrained continuous phase of the fluid gel may also contain some hydrated/partially hydrated unassociated rigid polymer chains, which provide some lubrication by preventing contact between the ball and disk surfaces.

The friction coefficient of the fluid gels ran parallel to that of water until 200 mm s^{-1} when friction drastically reduced. Above this entrainment speed it is likely a layer of mono particles is established between the ball and PDMS disk surfaces aiding lubrication. This behaviour has been previously described by De Vicente *et al.* (2010) for confinement of neutralised carbopol particles to a reduced friction layer. (de Vicente, Stokes, & Spikes, 2006)

When 10 % sunflower oil was added to the continuous phase of the fluid gels, a reduction in the boundary friction was evident at low speeds, friction values similar to sunflower oil were observed, as a result of the additional lubricant in the continuous phase. Once in the mixed regime the friction values tended towards those of the sunflower oil, strongly indicating that the addition of low amounts of sunflower oil gave oil like friction properties to the fluid gel both in the boundary and mixed sections of the experiment (**Fig. 7 inverted triangles**). The measurement of friction coefficient showed that if oil was added to the continuous phase of the fluid gel, the system closely resembled an oil in water emulsion (Shown in **Fig. 8.** for comparisons) and the presence of the fluid gel particle became negligible as equivalent levels of friction could be obtained without the need to exceed the sunflower oil content of the formulation by more than 10 %.

The comparison of the friction coefficient when the fluid gels continuous phase had the addition of 10 % sunflower oil and when 10 % of a water in oil emulsion (stabilised using triglyceride) is shown in **Fig. 8.**

The low values of boundary friction shown for both the w/o emulsion (**Fig. 8.** inverted triangles) and stabilised emulsion/fluid gel mixtures (**Fig. 8.** triangles), highlighted that a fluid gel mixed with a w/o emulsion could be used to reduce friction to a point close to sunflower oil. The stabilisation of w/o emulsions with a triglyceride shell around the dispersed water phase can be used to encapsulate water and allow formulations to be more suitable in moisture sensitive applications. The reduction in friction coefficient exhibited in fluid gel with 10 % triglyceride stabilised emulsion added to the continuous phase was the result of particles of emulsion and fluid gel with varying levels of deformability. The rigidity of the triglyceride-stabilised particles is thought to allow them to be rapidly entrained in the contact between the ball and disk (illustrated in **Fig. 9**) at low entrainment speeds. The result of the particles entrainment being a decrease in deformation of the more compressible xanthan particles, reducing the contact area and lowering the measured friction. The importance of deformability of the fluid gels particles was in agreement with the work of Garrec *et al.* (2013) who in kappa carrageenan

systems reported an increase in friction coefficient when particles become more deformable as a result of reducing surface separation. (Garrec & Norton, 2013) The entrainment of ridged particles aids the system in quickly overcoming initial boundary friction, resulting in lubrication behaviour, which mimics that of sunflower oil.

In order to verify the proposed mechanism of particle entrainment, both xanthan gum fluid gels and the fluid gel mixed with 10 % (wt/wt) of the stabilised w/o emulsion, were subjected to rolling lubrication under loads between 0.5 and 6 N. The results are shown in **Fig. 10**.

The friction coefficient in xanthan gum fluid gels systems were seen to rise as the entrainment speed increased under all loads (shown by the closed symbols in **Fig. 10**). This rise was likely due to initially the particles of the fluid gel being excluded from the contact point until the accumulation of excluded particles became sufficient to overcome the load on the ball. **Fig. 10** shows that the entrainment speed needed to overcome this exclusion was reduced from 2.3 mm s^{-1} to 1.5 mm s^{-1} when the load was reduced from 6 N to 3 N (indicated by the blue arrows in **Fig. 10**). Under very low loads (0.5 N) the increase in friction and overall lubrication was seen to be much lower as the fluids and particles easily overcame the resistance to entrainment between the ball and the disk. The increase in lubrication as a result of the addition of the stabilised emulsion particles was also evident from the results, where it can be seen that overall lubrication was increased at all levels of load tested. The initial increase in friction when the load on the ball was equal to 6 N was as result of the exclusion of both the fluid gel and emulsion particles at low speeds. Under lower loads (3 N) the absence of the earlier increase in friction is in agreement with the proposed entrainment method. Under rolling conditions the deformable xanthan particles may initially be separated from the continuous phase as the continuous phase is entrained between the ball and PDMS disk, preventing the particles from having an effect on lubrication. On the other hand the smaller size and increased uniformity and hardness of the stabilized emulsion particles increased the likelihood of entrainment and subsequent lubrication as the contact point could be quickly parted. A similar dependence of the particle size on the friction as well as the resultant perceived fatty mouth feel has also been reported previously by de Wijk *et al.* (2005) for custard/starch desserts under similar rolling condition. (de Wijk & Prinz, 2005) Beyond the boundary regime the lubrication properties of the fluid gel with stabilised emulsions/fluid gel mixtures became equivalent to those of a sunflower oil/water mixture, strongly indicating that the system behaved like an oil in water emulsion with the added benefit of 30 % (by mass) of the additional oil being replaced with low calorie water.

4. Conclusion

This investigation has shown that xanthan gum fluid gels are formed by the application of shear forces during cooling through the conformational transition. The addition of 10 % (wt/wt) sunflower oil to the continuous phase of the xanthan gum fluid gels was shown to reduce the measured friction

1 coefficient, and the values of friction were similarly reduced by the addition of 10 % of an w/o
2 emulsion stabilised by triglycerides to the continuous phase. The increased lubrication was a result of
3 ridged emulsion particles parting the surface and limiting deformation of the fluid gel particles, and
4 confirmed by studying the dependence of the friction coefficient on the load exerted on the surfaces.
5 Overall composite mixtures of fluid gels and triglyceride stabilised w/o emulsions have been shown to
6 be a viable route to obtaining lubrication behavior similar to sunflower oil at 7 % sunflower oil
7 content.

8

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Figure 1. Schematic representation of the pin stirrer unit (a) sample inlet (b) sample outlet (c) inlet for thermal jacket (d) thermal jacket outlet

Figure 2. Bright field images of xanthan gums produced under shear (a) after hydration at 20 °C (b) by hydrating at 80 °C and sheared whilst cooling. * denotes the xanthan particle.

Figure 3. Storage and loss modulus of xanthan gum gels produced under shear conditions as the temperature is reduced from 80 °C to 20 °C (circles) and isothermally at 20 °C (triangles). All measurements made at 20 °C.

Figure 4. Gel viscosity formation curves of xanthan gum formed under shear (500 s^{-1}) at 20 °C (solid circles) and as the temperature was reduced from 80 °C to 20 °C (open triangles).

Figure 5. Viscosity response as a function of shear rate for gels formed whilst cooling from 80 °C (filled circles) and gels formed isothermally at 20 °C (open circles). All measurements made at 20 °C.

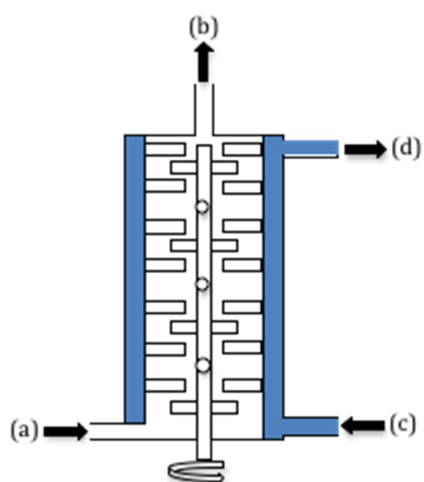
Figure 6. Confocal imaging of (a) Triglyceride fat shell emulsion dyed with Nile red (b) Sunflower oil (green) oil and water emulsion, (c) and Xanthan gum fluid gel particles (black voids)

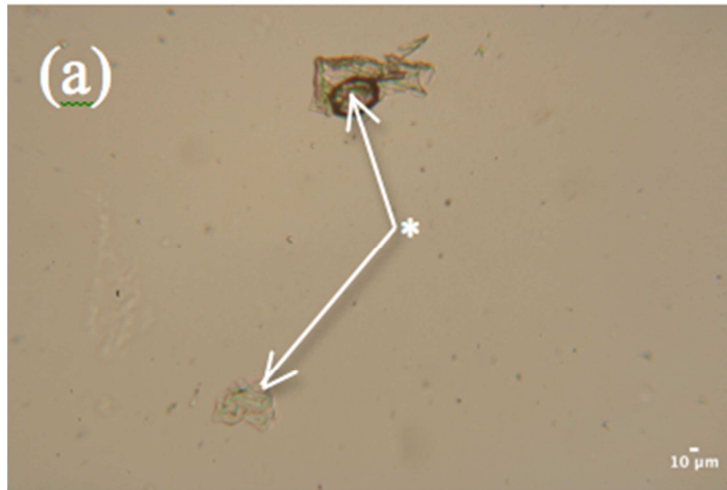
Figure 7. Comparison of Stribeck curves for xanthan gum fluid gels and fluid gel oil suspension, limit of boundary friction highlighted by blue arrows.

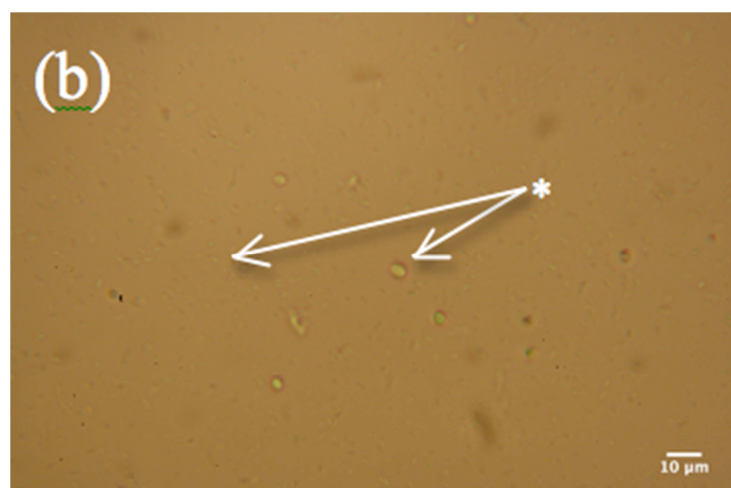
Figure 8. Comparison of Stribeck curves for xanthan gum fluid gels and fluid gel particulate emulsion suspension

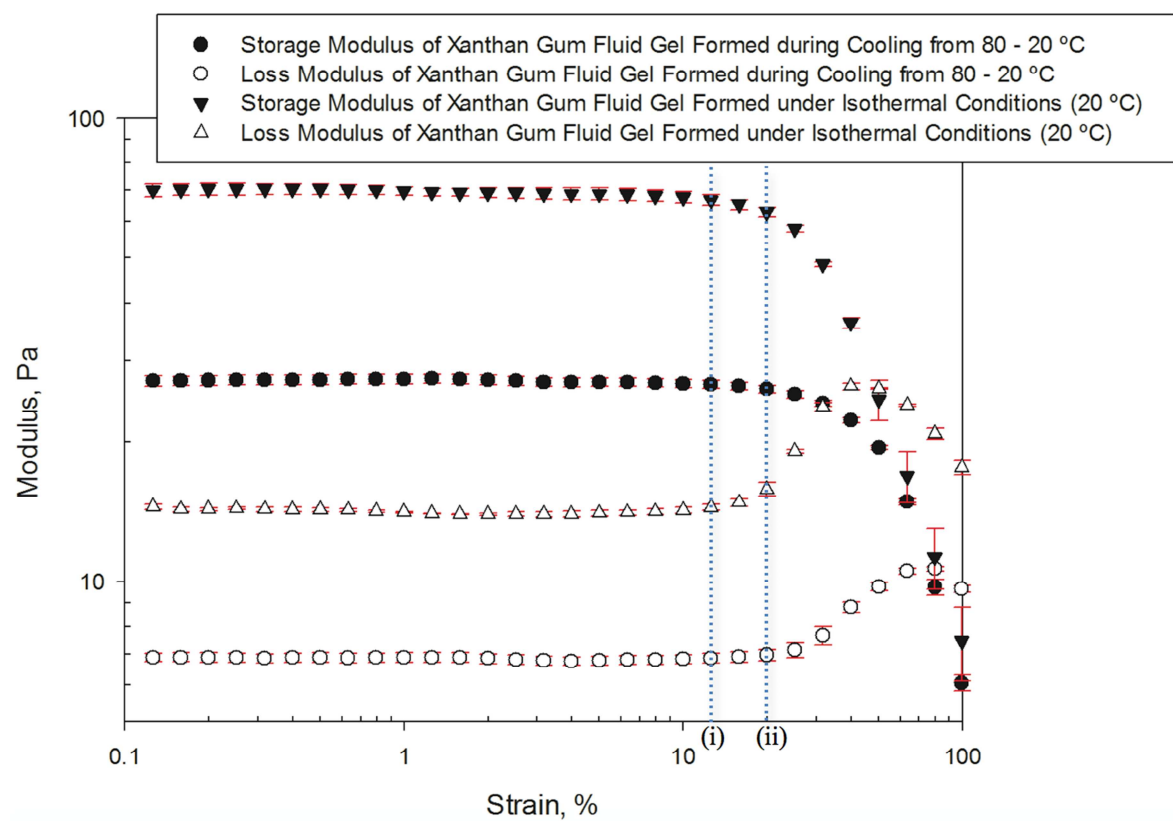
Figure 9. Schematic of the behaviour of fat replacement fluid gels under increased entrainment speeds (a) fluid gels (b) 10 % triglyceride stabilised emulsion added to the continuous phase of the fluid gel

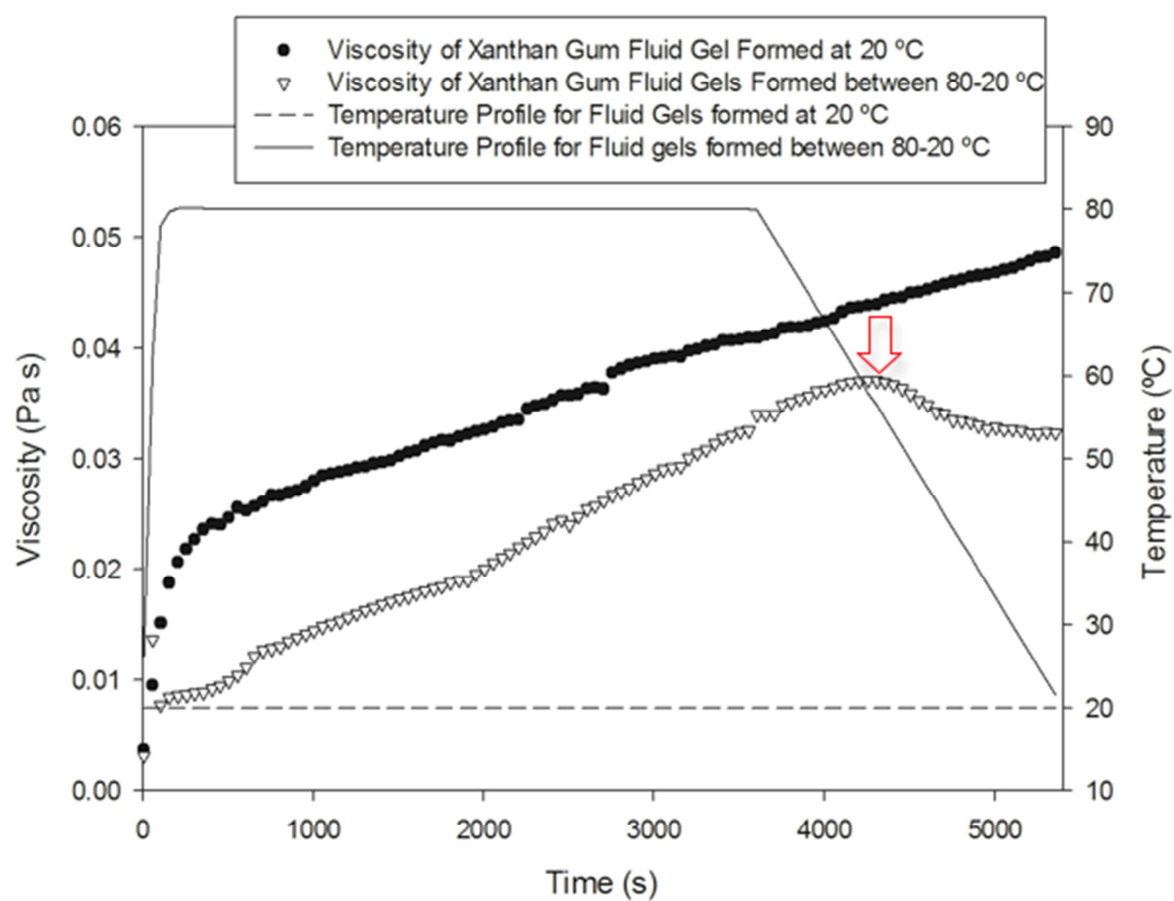
Figure 10. Comparison of the lubrication behaviour under varying loads of xanthan gum (closed symbols) and xanthan gum/triglyceride stabilised emulsion mixtures (open symbols)

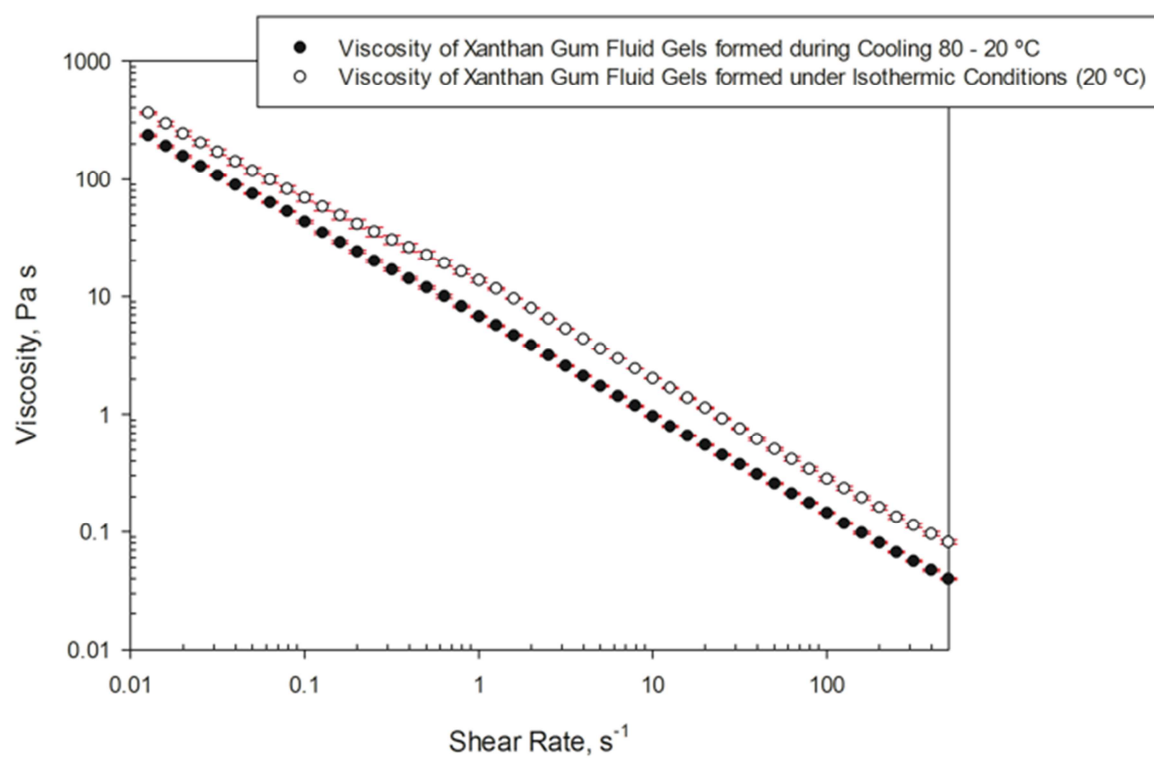


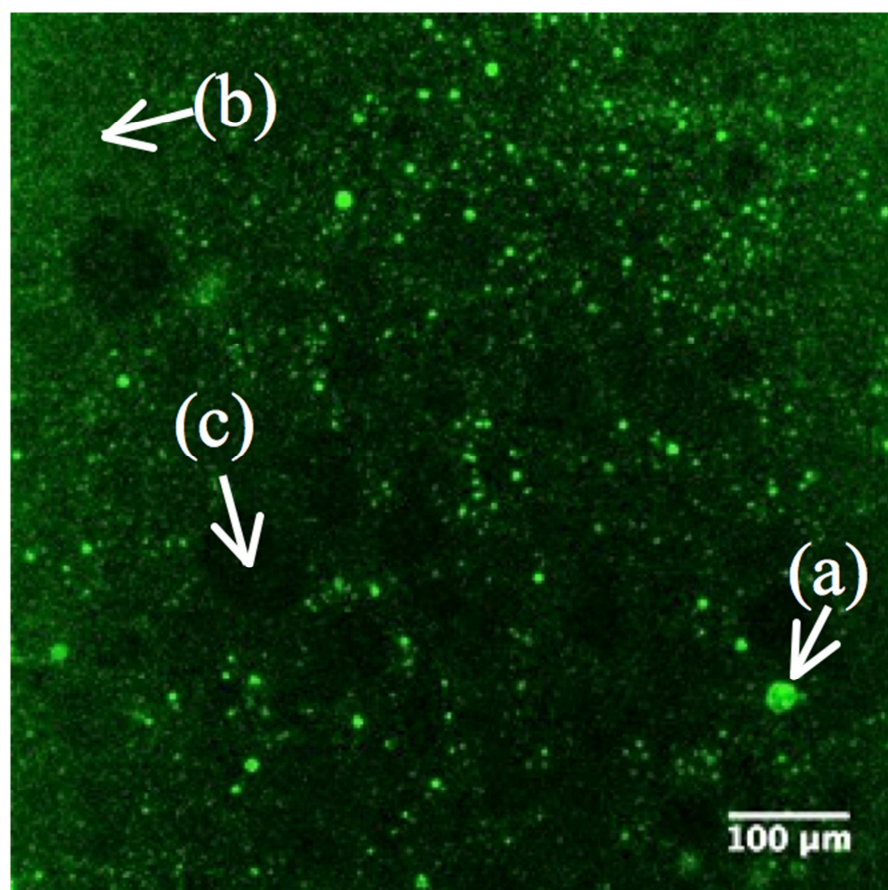


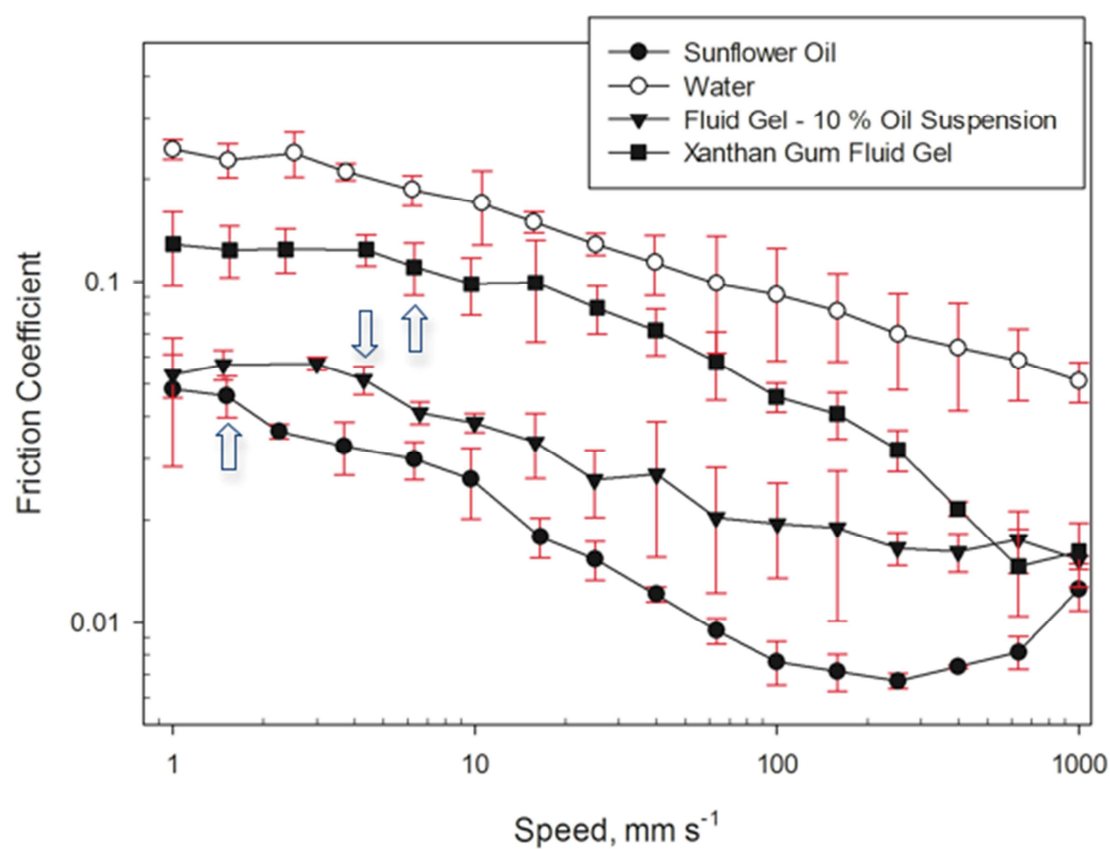


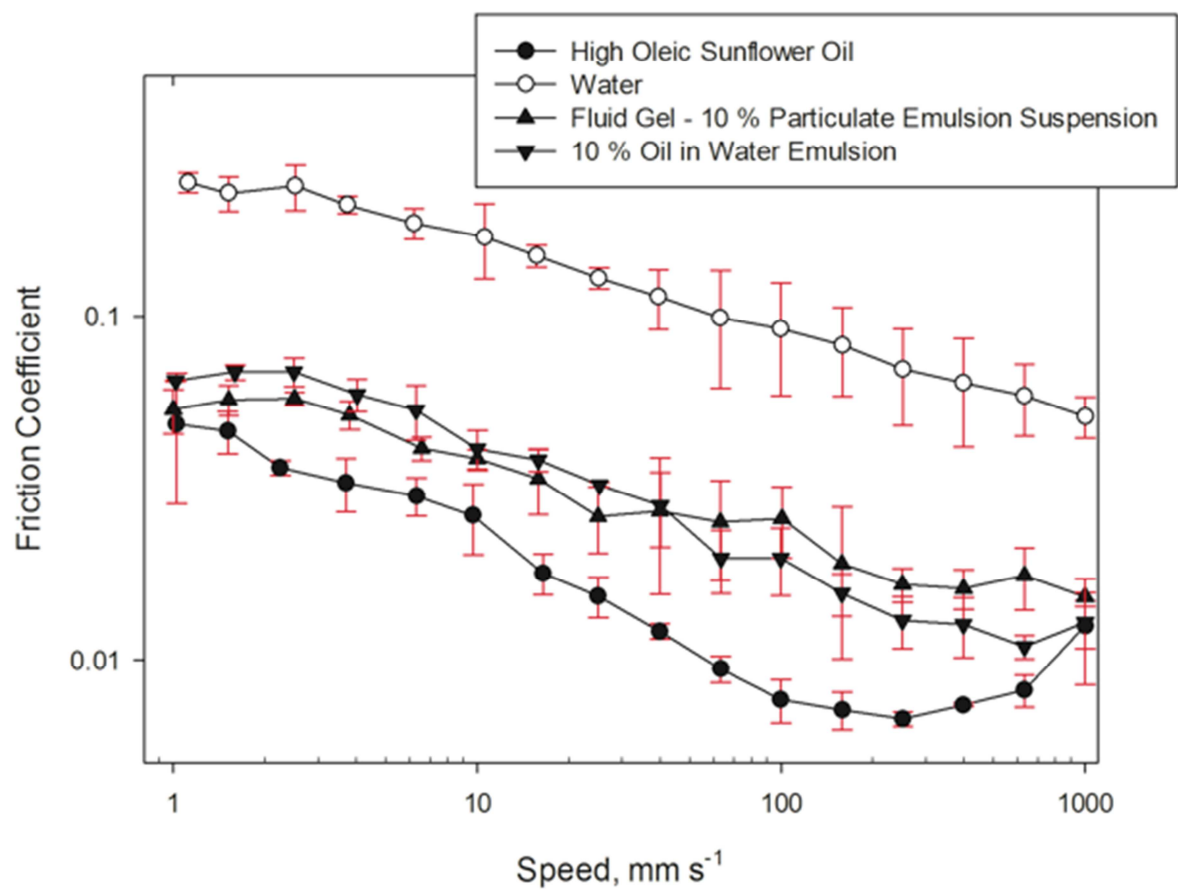


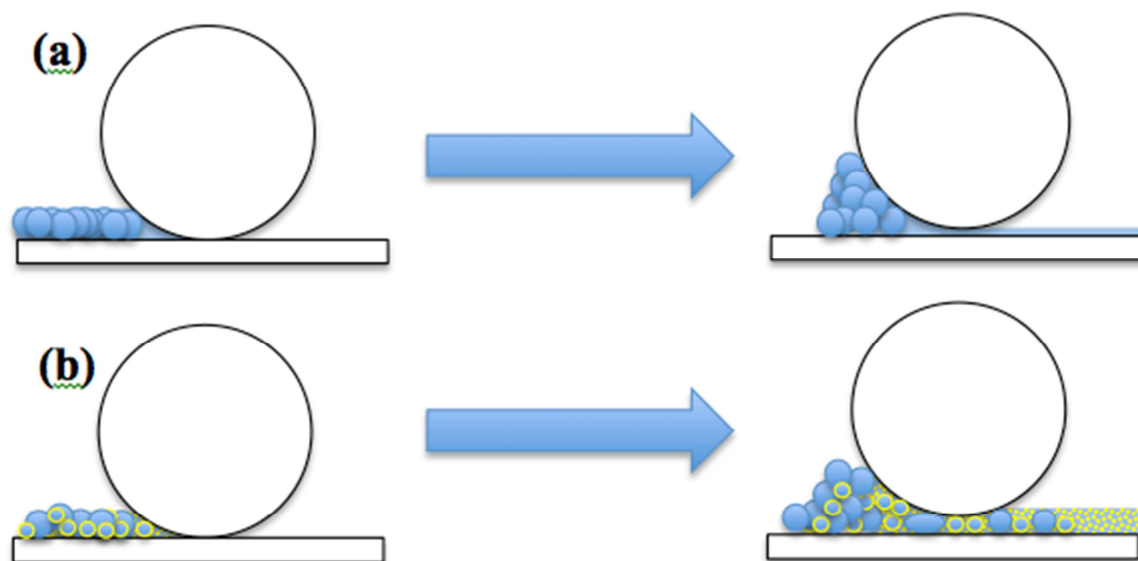


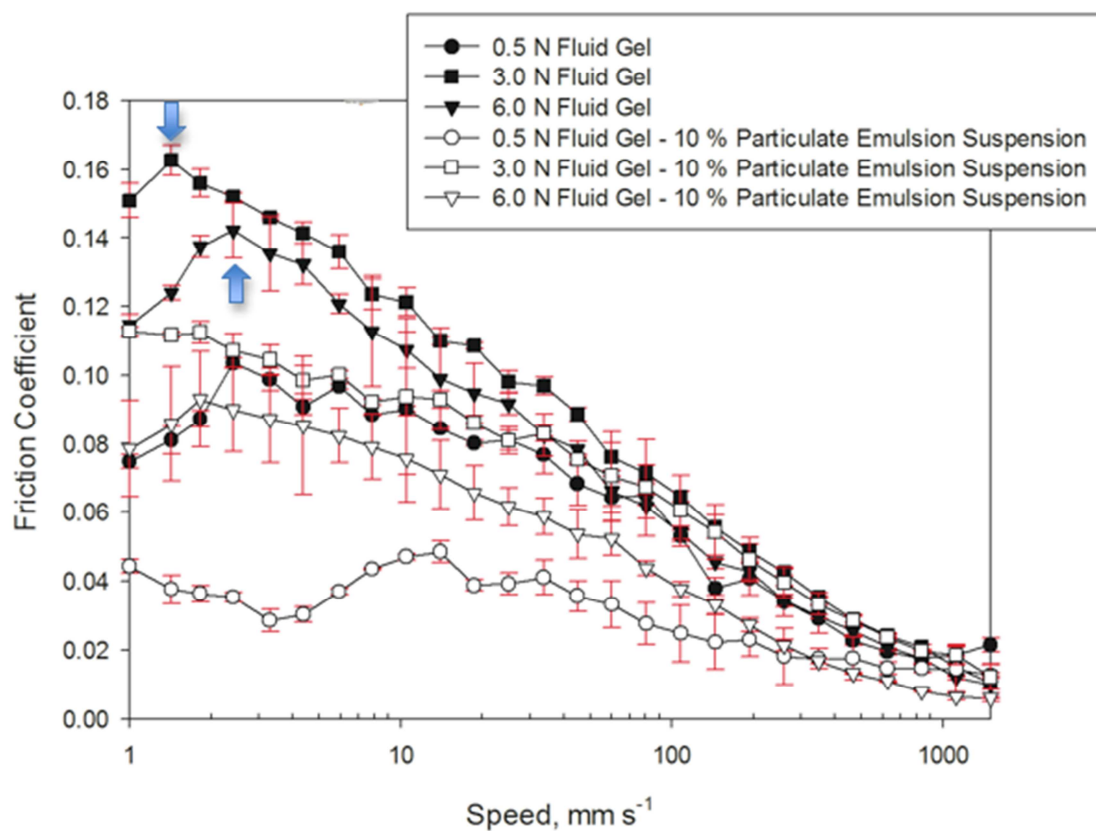












Highlights

- Xanthan Gum fluid gels have been produced
- Inclusion of sunflower oil in fluid gel particles increase friction
- Addition of triglyceride stabilised water in oil emulsions to the continuous phase lower friction